Nanoscale self-organization reaction in Cu-Ag alloys subjected to dry sliding and its impact on wear resistance

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Abstract

Two-phase Cu₉₀-Ag₁₀ alloys are subjected to dry-sliding wear using pin-on-disk testing at room temperature with either a bronze or a martensitic stainless steel as counterface material. Thermal annealing prior to wear testing is used to vary the initial Ag-rich precipitate size in the Cu-rich matrix from ≈ 30 to 260 nm. The wear debris and the sub-surface microstructure are characterized by scanning and transmission electron microscopy. For large enough initial precipitate size, wear induces the spontaneous formation of alternating Cu and Ag nanolayers, and this chemical nanolayering correlates with a significant reduction in wear rate. This correlation is analyzed by considering the role of chemical nanolayering on third bodies and on the mechanical properties of the near-surface microstructure.

Keywords: dry sliding, Cu-Ag alloys, self-organization, nanolayers

1. Introduction

During sliding wear of metallic materials, regions close to the contacting surfaces are subjected to large plastic deformation. This deformation modifies the microstructure and thus the properties of the worn regions, for instance increasing the hardness through work hardening and grain size reduction [1]. These microstructural modifications should therefore be considered when choosing or designing materials for wear-resistant applications. The challenge is that the worn surfaces constitute non-equilibrium, dissipative systems, which exchange energy and matter with their environment, namely the opposing surfaces, liquid and solid lubricants when present, and gases near the contact area. Such materials systems which are sometimes referred to as driven [2], typically reach stable steady states. The exact nature of these steady states, and in the case of wear, their corresponding wear rate, is difficult to predict since, unlike thermodynamics for equilibrium systems, there is no general framework for phase and microstructural evolutions of non-equilibrium systems. Furthermore, small variations in control parameters, such as temperature, sliding velocity, and load can have dramatic impact on wear regimes and wear rates, as illustrated by the presence of boundaries in the wear maps introduced by Lim and Ashby [3].

Despite these many challenges, an attractive feature of driven materials is their tendency to self-organize in response to the external forcing into microstructural patterns on a nanometer length scale [4]. This capability to self-organize thus offers a useful control parameter in the design self-adaptive materials. The potential of this approach for reducing friction and wear has been illustrated for instance by Erdemir [5], Scharf and Prasad [6], with the spontaneous formation of lubricious oxides at sliding interfaces, and by Voevodin and coworkers [7], with “chameleon coatings” where friction induces a transition from sp^3 to sp^2 bonding in diamond-like carbon. In the present work, we consider wear-induced chemical nanolayering, a distinct self-organization reaction, which was recently uncovered in Cu-Ag alloys subjected to dry-sliding wear using pin-on-disk tests [8]. Near the wear surface, the initially equiaxed microstructure, which consisted of isolated Ag-rich precipitates in a Cu matrix, spontaneously evolved into alternating

nanolamellae of Cu-rich and Ag-rich phases. It was furthermore reported that when these nanolamellae existed all the way to the sliding surface the wear rate was reduced by factors ranging from 2 to 16, depending on the counter surface.

The present study extends our previous results [8], focusing here on the origin of wear reduction by chemical nanolayering in Cu-Ag alloys subjected to dry sliding. After presenting the experimental methods in Section 2, wear debris and wear microstructures are analyzed in Section 3, and the correlation between sliding-induced nanolayering and wear reduction is discussed in Section 4.

2. Experimental methods

We recall here the methods employed to fabricate the Cu-Ag alloys, subject them to dry sliding, and to characterize the samples before and after wear. Additional details are found in ref. [8].

2.1 Synthesis of materials

Powders of Cu and Ag, with a nominal composition of Cu₉₀Ag₁₀ in at. %, were alloyed by high-energy ball milling using a SPEX 8000 mill in a purified argon glove box. The ball-milled powders were then transferred to a hot press in an argon atmosphere, and compacted into small cylinders at 573 K with a 1 GPa load under a high vacuum (2×10^{-6} Pa). During this procedure, Ag precipitates formed with a volume-averaged diameter of 32 nm. The as-pressed samples were further annealed at 723, 873 and 1023 K for 1 h in an argon tube furnace, leading to volume-averaged precipitate diameters of 58 nm, 122 nm and 262 nm respectively, as determined from scanning transmission electron microscopy (STEM) images [9].

2.2 Pin-on-disc wear testing

Discs, 3 mm in diameter and 1.5 mm thick, were cut from the pressed and annealed samples by electrical discharge machining (EDM). These discs were then mounted onto a bronze pin also of 3 mm in diameter with super glue. The pins were then subjected to dry

sliding wear using a Koehler K93500 pin-on-disc tester in air under 9.8 N load, at a relatively low sliding velocity of 0.25 m/s to minimize flash temperatures, but using sliding distances long enough, up to 450 m, to measure wear rates in the steady-state regime. Two different counterface materials were used for the pin-on-disc tests, a martensitic stainless steel SS440C disc, with a Rockwell scale C hardness value of ≈ 60 HRC and a tensile strength of 2.2 GPa, and a Cu-Ni-Sn bronze with a hardness of ≈ 32 HRC and a tensile strength of 950 MPa. Prior to testing, the contacting surfaces of the sample and disc were polished to achieve an average surface roughness (Ra) less than 200 nm. During the wear test, the friction coefficient and the linear displacement vs. time curves were recorded. The wear rates have been determined by measuring the pin weight loss. Three independent wear tests were conducted for each metallurgical state of the Cu-Ag samples and for each counterface material.

2.3 Materials characterization

Scanning electron microscope JEOL-7000F equipped with energy dispersive X-ray analysis (EDX) was utilized to characterize the morphology of the worn surface and the size and composition of the wear debris. Transmission electron microscopy (TEM) and scanning TEM (STEM) were used to characterize the alloy microstructures before and after wear. For relating the microstructures to the wear test geometry, a laboratory frame of reference was defined by the sliding direction (SD), the transverse direction (TD) in the sliding plane, and the direction normal to the worn surface (ND). Cross-sectional TEM samples both parallel to sliding direction (ND-SD plane of view) and perpendicular to sliding direction (ND-TD plane of view) were prepared by focused-ion beam (FIB), lift-out technique. High-angle annular dark-field (HAADF) STEM imaging was employed to image the Cu and Ag distribution. In addition, conventional and analytical TEM were used to characterize the microstructures. The sample hardness was measured using a Hysitron TI-950 Triboindenter with a Berkovich diamond tip. The roughness of the sample surface before and after wear test was measured by a Sloan Dektak³ ST stylus surface profilometer.

3. Results

3.1. Wear rate and wear debris

The Ag precipitate size and hardness of the Cu₉₀Ag₁₀ samples are reported in Table 1, and their wear rate, coefficient of friction are reported in Table 2, and the surface roughness in Table 3, for both counterface materials. Table 1 shows that, as expected, the average Ag precipitate size was larger for the higher annealing temperatures, correlating also with a larger grain size, and thus with lower hardness. Several noteworthy observations are found in Table 2. As previously reported [8], the steady-state wear rate decreased as the Ag precipitate size was increased, a rather surprising trend considering that the samples with the larger Ag precipitates were softer. Moreover, the wear rate was much more impacted by the Ag precipitate size for the bronze counterface, where the wear rates for the as-compacted and 1023 K annealed samples differed by a factor ≈ 16 . For the SS440C counterface disk, the corresponding change was a factor of ≈ 2 . In contrast to these results, the friction coefficient (COF), see Table 2, and the roughness of the worn surfaces, see Table 3, were fairly constant for each counterface material, and showed little difference between the bronze disc and the SS440C disc.

The morphology of the pin surface after wear testing was similar for both counterface materials, as illustrated in SEM images shown in Figs. 1 and 2, with features of localized material flow and extrusion typical of adhesive wear in the presence of third body particles and films [10]. At higher magnification, however, differences between the two counterface materials become noticeable. Most notably, fine particles about a micron in size covered the surfaces worn against the SS440C disk, see Fig. 1(b,d), while the surfaces appeared smooth in the bronze case, see Fig. 2(b,d).

The counterface material had a much stronger impact on the wear debris. In the bronze case, debris particles displayed a flake-like morphology and they were fairly large, with flake length ranging from tens to hundreds of microns, as illustrated in Fig. 3(a,c). Furthermore, EDX analysis indicated that most of the wear debris contained Cu and Ag, although occasionally flakes consisting of Cu, Ni and Sn were detected, thus clearly

showing some material evolving from the counterface disk. In contrast to these large flakes, in the case of the SS440C disk, the wear particles were roughly equiaxed and much smaller, typically $\approx 1 \mu\text{m}$ in size, as seen in Fig. 4(a,c). Moreover, the composition of the debris included the alloying elements from the pin, Ag and Cu, as well as elements coming from the SS440C disk, as seen in Fig. 4 (b,d). These difference in wear debris morphology and composition provide a first insight into the origin of the much larger wear rates measured in the bronze case (Table 1) than in the SS440C case (Table 2).

3.2. Wear-induced microstructures and nanolayering

We reported in ref. [8] that, for samples containing Ag precipitates whose initial size was large, i.e., $d_p \geq 120 \text{ nm}$, sliding wear induced the spontaneous formation of a nanolayered structure with lamellae composition alternating between a Cu-rich phase and a Ag-rich phase. In contrast, for smaller initial precipitate size, $d_p \leq 60 \text{ nm}$, the topmost surface evolved into a Cu-Ag solid solution with equiaxed nanograins. The detailed TEM and STEM characterization of these microstructures was reported for the SS440C counterface material in [8]. We show here that similar microstructures are observed in the case of the bronze counterface. In particular, for the samples pre-annealed at **1023 K**, the nanolayered structure is clearly seen in Fig. 5, both in bright field imaging mode, and in HAADF-STEM (or Z-contrast) mode. In the latter case, owing to the much larger atomic number of Ag over Cu, the Ag-rich lamellae appear brighter than the Cu-rich lamellae. The lamellae thickness increased from $\approx 10 \text{ nm}$ just below the wear surface to $\approx 20 \text{ nm}$ at a depth of $4.5 \mu\text{m}$. The selected area diffraction pattern, Fig. 5(b), indicates also that these layers exhibit significant texturing, with $(111)_{\text{Cu}}/\text{ND}$. This orientation is typical of shear textures in fcc metals [11].

In the case of samples with smaller initial Ag precipitate size, the top portion of the worn microstructure was a Cu-Ag solid solution, as illustrated by the uniform Z contrast in Fig. 6(a). At a depth of $\approx 2 \mu\text{m}$, nanolayering was observed, see Fig. 6(b), and at a depth of $\approx 4 \mu\text{m}$, a fairly sharp transition was seen between the nanolayered region, seen in the upper part of Fig. 6(c), and the original equiaxed Ag precipitate structure, seen in the

lower part of Fig. 6(c). This sequence of microstructures is also observed in bright field images, Fig (7). In particular, the formation of a solid solution just below the sliding surface is confirmed by the electron diffraction pattern, which shows the presence of only one fcc phase, see Fig. 7(a). In contrast, $\approx 4 \mu\text{m}$ below the wear surface, the diffraction pattern confirms the co-existence of two fcc phases, see Fig. 7(c).

One important difference between the wear microstructures produced by the bronze and the SS440C counterface materials is that in the bronze case there is no detectable transfer layer at the top of the pin. As seen in Figs. (5-7), the Cu/Ag nanolayered structure, for the sample pre-annealed at 1023 K, or the Cu-Ag solid solution, for the sample pre-annealed at 723 K, are found immediately below the Pt layer deposited during FIB sample preparation, which is thus a marker of the wear surface at the end of the wear test. In contrast, in all the samples worn against SS440C disk, the surface is covered by a transfer layer, whose thickness varies from place to place, from a fraction of a micron to several microns, as illustrated in Fig. 8. Structural and chemical analysis of this layer by TEM and TEM-EDX indicated that it is an equiaxed nanocomposite, consisting of Fe-rich oxide and Cu-Ag grains, with grain sizes $\approx 10 \text{ nm}$ [8]. It is interesting to note that there is some large scale mixing between this nanocomposite transfer layer and the Cu/Ag nanolayered structure underneath it, as seen in Fig. 8(b).

4. Discussion

The above results, and those earlier reported in ref. [8], indicate that the presence of chemical nanolayering just below the wear surface correlates with an increase in wear resistance, for both counterface materials, as seen in Table 2. When the initial Ag precipitate size is too small, e.g., $d_p \leq 60 \text{ nm}$, nanolayering is partly present, but not at the top of the worn surface, where a Cu-Ag solid solution becomes stabilized instead. It is important to note that this nanocrystalline solid solution is not as wear-resistant as the chemically nanolayered microstructure, as seen in Fig. 9, despite the fact that the former nanostructure is much harder, $\approx 5 \text{ GPa}$, than the latter one, $\approx 3\text{-}4 \text{ GPa}$, as reported in ref. [8], where nano-indentation was used to measure hardness profiles from the various Cu-

Ag alloys discussed here. This inverse correlation between wear resistance and hardness is clearly in contradiction with Archard's law. In order to resolve this paradox, we discuss the possible impacts of nanolayering on friction and on third body materials. We then discuss the role of nanolayering on wear resistance using the concept of the tribological circuit, and the role of the initial Ag precipitate size on nanolayering.

4.1 Role of nanolayering on friction

The results presented in Section 3 indicate that chemical nanolayering has little to no impact on friction. Indeed, the coefficient of friction measured for each counterface disk was independent of the initial Ag precipitate size, see Table 2, and thus independent of the presence or absence of chemical nanolayering at the top of the worn surface. Furthermore the morphology, the size, and the chemical nature of the wear debris were also independent of the initial Ag precipitate size (although they were very different for the two counterface materials, a point that will be discussed below). This absence of effect of chemical nanolayering on friction is also consistent with past works on the reduction of friction by thin metallic films deposited in substrates. As first demonstrated by Bowden and Tabor [12] and confirmed later in additional studies [13, 14], the thickness of these thin metallic films needs to exceed some minimum value, typically 100 nm to 1 μ m, for inducing a significant reduction of the friction coefficient. Since the Ag lamellae formed by nanolayering are only $\approx$ 10 nm thick near the wear surface, one would not expect any significant reduction of the friction force from those layers. It is thus concluded that the reduction of wear imparted by nanolayering cannot be explained by its effect on friction, and that other contributions needed to be considered.

4.2 Role of nanolayering on third body material

One of the limitations of Archard's law is that it ignores the role of the third body material formed at the sliding contact between the two first bodies, whereas it is now well established that this third body plays an essential role on wear resistance [10, 15]. The first question is thus to identify the nature of the third body material. The results

presented in Section 3 makes this identification possible. Since differences in wear debris and worn surface microstructures are observed for the two counterface materials used in the present work, it is necessary to consider them separately in this discussion. In the case of the bronze counterface material, the top of the worn Cu-Ag pins contains only Ag and Cu, either as Cu/Ag nanolayers (Fig. 5) or as a Cu-Ag solid solution (Fig. 6), and the wear debris flakes consist only of Cu and Ag (except for a few bronze flakes). Furthermore the Cu-Ag flakes appear to have formed by compaction of many smaller elements, whose thicknesses are a few microns or less, and thus similar to the thickness of the regions undergoing nanolayering, see Figs. (5-7). These observations point to a scenario where wear particles break off from the top few microns of the worn microstructure, where nanolayering is present. In addition, the morphology of the wear surface, shown in Fig. 2, indicates that there is considerable compaction and extrusion of the surface material, suggesting that the wear particles were ejected from the wear track only after significant re-circulation in the contact. We conclude that the Cu-Ag nanolayered structure is playing the role of a third-body in this case, by accommodating the velocity difference between the two first bodies.

We turn then to the tests performed against the SS440C counterface material. The chemical make-up of the wear particles and their morphology, see Fig. 4, suggest that they were formed by detachment from the oxide-metal nanocomposite transfer layer. In contrast to the bronze counterface case, however, the Cu-Ag nanolayered structure is only marginally present in the wear debris. The nanolayered material found in the wear debris may in fact come from the transfer film since it can locally intermix with the nanolayered structure, as illustrated in Fig. 8(b). We thus conclude that, when using SS440C as counterface material, the oxide-metal nanocomposite transfer layer is acting as the main third body, in contrast to the bronze case.

4.3 Role of nanolayering on the tribological circuit

Now that the nature of the third body has been identified for both counterface materials, it is useful to consider the tribological circuit proposed by Berthier [16] and his coworkers

[17] to analyze the effect of the third body on wear. This circuit involves three main stages, first the generation of third body material by material detachment from the surfaces of the first bodies, second the circulation and trapping of this third body in the contact zone, and third the ejection from the contact zone of third body particles, which then become wear debris. The coefficient of friction is largely determined by the second stage, and since we already concluded that nanolayering has no impact on friction, we focus our attention to the first and the third stages of the tribological circuit.

Neglecting the re-circulation of third body particles in and out of the sliding contact, Fillot et al. [18, 19] developed a simplified approach which predicts that under steady-state conditions, a stable thickness of third body material should form, and that this value results from a balance between the rate of detachment of third body particles from the first bodies and the rate of ejection of third body particles from the sliding contact, see for instance Fig. 15 in ref. [19]. In this approach, the physical situation assumed in Archard's law is one with zero third body thickness, and it yields the maximum wear rate. The improvement brought about by the third body is a complex function of the dependence of the detachment and ejection rates with the thickness of third body and with its physical properties, in particular adhesion between third body particles [18, 19]. Since it is unlikely that the ejection rate would be significantly different for a Cu-Ag solid solution and for a Cu-Ag nanolayered structure, it is reasonable to conclude that the primary beneficial effect afforded by chemical nanolayering should reside on its impact on the detachment rate of material from the first bodies, that is in the first stage of the tribological circuit.

We propose that the presence of nanolayering can reduce the generation rate of third body material for two distinct reasons. First, the Cu/Ag nanolayered structure may have a lower shear strength than the Cu-Ag solid solution and than the initial equiaxed Cu-Ag composites, thereby increasing the localization of the plastic deformation at the very top of the wear surface; and second the nanolayered structure may possess an increased fracture toughness, owing to its nanolaminate structure with layers of a more compliant phase (Ag) alternating with layers of a stronger phase (Cu); the many Cu/Ag interfaces

could effectively deflect cracks and thus reduce the thickness of the pieces that detach from the first body surface to become third body.

Considering first the question of the shear strength of metallic nanolayered structures, we note that the shear strength of artificial nanolaminates depends critically on the details of the crystallography of the interfaces. This point can be illustrated by considering the case of Cu/Nb nanolaminates, for which different fabrication routes are available, and result in different interface characteristics and different mechanical properties. Cu/Nb nanolaminates produced for instance by physical vapor deposition (PVD) have much lower shear strength than those synthesized by accumulative roll bonding (ARB) [20]. This difference has been assigned to the fact that PVD Cu/Nb interfaces are characterized by a Kurdjumov-Sachs (KS) orientation relationship and a $(111)_{\text{Cu}}// (110)_{\text{Nb}}$ habit plane, which allows for easy glide of interfacial dislocations in the interface habit plane. In contrast, in ARB Cu/Nb nanolaminates, the dominant interface habit plane is $(112)_{\text{Cu}}// (112)_{\text{Nb}}$, and thus dislocation glide in this habit plane is severely restricted [21]. Molecular dynamics simulations confirmed this analysis, indicating that the interfaces shear strength is much larger in the $(112)_{\text{Cu}}// (112)_{\text{Nb}}$ case, ≈ 1 GPa, compared to ≈ 0.3 GPa for the $(111)_{\text{Cu}}// (110)_{\text{Nb}}$ KS interfaces [22, 23]. In the case of wear-induced Cu/Ag nanolayering, we indicated earlier that the chemical nanolayering was accompanied by the development of a crystallographic texture, with the predominant alignment of Cu and Ag (111) planes with the sliding plane, as attested by the selected area diffraction pattern in Fig. 5(b). This preferred orientation is in fact one of the characteristics of the so-called A-type shear texture components in fcc metals, texture components that are often found in materials subjected to simple shear deformation [11]. It is thus likely that the chemical nanolayering results in a lower shear strength, in particular compared to the Cu-Ag solid solution formed at the wear surface in the case of samples pre-annealed at 723 K. One possible method to quantify the interface shear strength would be to perform compression tests in situ in a TEM on sub-micron pillars extracted from worn surfaces, as this technique has been successfully used to determine the shear strength of various metallic multilayered materials [24].

We consider now the possible improvement in fracture toughness imparted by wear-induced chemical nanolayering. This self-organization reaction generates a nanolayered structure with a high density of Ag/Cu interfaces, with a more compliant material, Ag, alternating with a stronger material, Cu. This type of layered composites can result in an increase in fracture toughness, as reviewed for instance in ref. [25]. Improvement on wear rate would then result from the deflection of surface cracks by the Cu/Ag multilayered structure, so that, regardless of their initial propagation direction, cracks are quickly forced to run parallel to the sliding surface, in turn minimizing the thickness of the pieces detaching from the first body surface. This picture is consistent with our observations of the wear particle sizes. For the case of the bronze disc, in particular, chemical nanolayering at the wear surface reduced the wear rate by a factor of ≈ 16 , see Table 2, while the lateral extension of the flaky wear particles were not significantly modified compared to the case where a Cu-Ag solid solution formed at the wear surface. This analysis would benefit from additional studies, aiming at measuring the fracture toughness of Cu/Ag nanolayers, and at imaging the third body dynamics, in particular using in-situ imaging techniques [26, 27].

4.4 Role of initial Ag precipitate size on nanolayering

One last point of discussion is the role of heat treatment prior to the wear tests on nanolayering. This heat treatment is used to vary the initial Ag precipitate diameter, from ≈ 30 nm in the as-pressed state to ≈ 260 nm after annealing for 1 hr at 1023 K. We first discuss the stabilization of a Cu-Ag solid solution at the wear surface for the as-pressed and 723 K pre-annealed samples. We note that this solid solution would be unstable at thermodynamic equilibrium, owing to the immiscibility of Cu and Ag. The stabilization of a solid solution during wear was however rationalized in ref. [8] by noting that severe plastic strain could force moderately immiscible elements such as Cu and Ag into a solid solution [28-30]. Past studies on metallic materials and alloys such as Cu [1, 31], Cu-Ag eutectic [32], and bronze [33], have reported that during dry sliding pin-on-disk wear tests the plastic strain increases approximately exponentially upon approaching the wear surface. In contrast, the plastic strain required to dissolve Ag precipitates increases only

linearly with the precipitate size [9, 34]. Consequently, for small enough initial Ag precipitates, the region the closest to the surface will form a Cu-Ag solid solution. This forced dissolution can even be used to estimate a minimum plastic strain experienced by the wear surface; by comparison with dissolution induced by high pressure torsion (HPT) of bulk samples, it was concluded in ref. [8] that the surface plastic strains exceeded ≈ 100 .

As the size of the initial Ag precipitates is increased by increasing the pre-annealing temperature, the plastic strain imposed by wear will eventually cease to be sufficient to force the mixing of Ag and Cu into a solid solution. It is thus expected that, in that case, wear would produce a Cu/Ag nanocomposite near just below the first body surface. It is however intriguing that this composite self-organizes into alternating Cu-rich and Ag-rich nanolayers. Additional experiments reveal that the strain path plays an important role: similar nanolayered structures were observed in the same Cu-Ag alloys subjected to high-pressure torsion at room temperature [8], but not during ball milling. Ball milling resulted only in the formation of nearly equiaxed nanocomposites [35]. These differences can be rationalized according to the main deformation modes in these different processing techniques, namely simple shear in sliding wear and HPT, compared to complex triaxial stress states in ball milling. As proposed in ref. [8], the spontaneous formation of this nanolayered structure thus appears to require a large simple shear deformation, in an alloy system where co-existing phases can co-deform. This self-organized chemical nanolayering can be seen as an extension of the crystallographic nanolayering that has been observed in some unary systems, e.g., Cu, Al, Ni, subjected to large simple shear deformation [36-38].

5. Conclusion

Two-phase Cu-Ag alloys were subjected to dry sliding via pin-on-disk wear testing at room temperature, using two counterface materials, a Cu-Ni-Sn bronze and a SS440C martensitic stainless steel. Detailed structural and chemical analysis of wear debris and worn surfaces was carried out using scanning and transmission electron microscopy.

While the wear debris particles were quite different in size and chemical composition for these two counterfaces, they matched directly the microstructures found in the top micron of the wear surfaces in each case. In both cases also, wear surface morphology provided clear evidence for the presence and role of third body. The initial diameter of Ag precipitates in the Cu matrix, which was varied by thermal annealing before the wear tests, was found to have a profound impact on the wear resistance. For large enough Ag precipitates, wear led to the spontaneous formation of nanolayers alternatively enriched in Cu and Ag just below the wear surface. This self-organization reaction reduced the wear rate by a factor up to 2 for the SS440C counterface and up to 16 for the bronze counterface. Three possible contributions of chemical nanolayering toward the improvement of wear resistance were considered, namely a reduction in friction, a reduction in shear strength and an increase in fracture toughness of the near surface material. It was concluded that the first contribution was negligible since the coefficient of friction was unaffected by the presence of nanolayers, as expected for the small thickness $\approx 10\text{-}20$ nm of these nanolayers. The microstructure of the layers, including their crystallographic texture, supported however the idea that both shear strength and fracture toughness should be modified in a way that promotes wear resistance. Additional experiments are proposed quantify these effects.

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Tables

Table 1 Precipitate size and hardness of two-phase Cu₉₀Ag₁₀ alloys as a function of the annealing temperature (annealing time of 1 h in all cases).

Annealing temperature (K)	Average Ag precipitate diameter d _p (nm)	Hardness (GPa)
As-pressed (573 K)	32	5.2
723 K	58	4.2
873 K	122	3.1
1023 K	262	2.5

Table 2 Coefficients of friction and wear rates of two-phase Cu₉₀Ag₁₀ alloys worn against bronze and SS440C disks as a function of annealing temperature (standard deviations are given in parenthesis).

Annealing temperature (K)	Coefficient of friction		Wear rate (mm ³ /(N·m))	
	bronze	SS440C	Bronze	SS440C
As-pressed (573 K)	0.57(0.024)	0.64(0.029)	2.33(0.15)×10 ⁻⁴	1.70(0.11)×10 ⁻⁵
723 K	0.52(0.015)	0.63(0.037)	1.38(0.09)×10 ⁻⁴	1.49(0.17)×10 ⁻⁵
873 K	0.51(0.017)	0.67(0.053)	8.64(0.12)×10 ⁻⁵	1.28(0.22)×10 ⁻⁵
1023 K	0.50(0.022)	0.64(0.041)	1.42(0.14)×10 ⁻⁵	9.12(0.18)×10 ⁻⁶

Table 3 Surface roughness of two-phase Cu₉₀Ag₁₀ alloys worn against bronze and SS440C disks before and after wear testing.

Annealing temperature (K)	Roughness (R _a) before wear (nm)		Roughness (R _a ') after wear (μm)	
	bronze	SS440C	bronze	SS440C
As-pressed (573 K)	121	149	1.16	1.97
723 K	147	141	1.43	2.19
873 K	138	137	1.57	2.43
1023 K	164	154	1.66	2.96

Figures

Fig. 1 Top-down SEM micrographs of the $\text{Cu}_{90}\text{Ag}_{10}$ samples worn against the SS440C disk; (a and b) samples pre-annealed at **1023 K** ($d_p = 262 \text{ nm}$); (c and d) samples pre-annealed at **723 K** ($d_p = 58 \text{ nm}$). The sliding direction (SD) is denoted by the arrow.

Fig. 2 Top-down SEM micrographs of the Cu₉₀Ag₁₀ samples worn against the bronze disk; (a and b) samples pre-annealed at 1023 K ($d_p = 262 \text{ nm}$); (c and d) samples pre-annealed at 723 K ($d_p = 58 \text{ nm}$). The sliding direction (SD) is denoted by the arrow.

Fig. 3 SEM micrograph of the wear debris and EDX spectrums of the $\text{Cu}_{90}\text{Ag}_{10}$ samples worn against the bronze disk; (a and b) samples pre-annealed at **1023 K** ($d_p = 262$ nm); (c and d) samples pre-annealed at **723 K** ($d_p = 58$ nm).

Fig. 4 SEM micrograph of the wear debris and EDX spectrum of the $\text{Cu}_{90}\text{Ag}_{10}$ samples worn against the SS440C disk; (a and b) samples pre-annealed at **1023 K** ($d_p = 262$ nm); (c and d) samples pre-annealed at **723 K** ($d_p = 58$ nm).

Fig. 5 ND-SD cross-sectional bright field TEM image (a), corresponding diffraction pattern (b) and STEM-HAADF image (c) of the $\text{Cu}_{90}\text{Ag}_{10}$ pre-annealed at 1023 K ($d_p = 262$ nm) and worn against a bronze disk.

Fig. 6 ND-SD cross-sectional STEM-HAADF images at various depths d below the sliding surface of Cu₉₀Ag₁₀ pre-annealed at **723 K** ($d_p = 58$ nm) and worn against a bronze disk. (a) $d = 0 - 1.5$ μm (the sliding surface is shown as a dashed line); (b) $d = 1.5 - 3$ μm ; (c) $d = 3 - 4.5$ μm .

Fig. 7. ND-SD cross-sectional bright-field images and corresponding diffraction patterns at various depths below the sliding surface of $\text{Cu}_{90}\text{Ag}_{10}$ pre-annealed at **723 K** ($d_p = 58$ nm) and worn against a bronze disk. (a) $d = 0 - 1.5 \mu\text{m}$, diffraction rings (1)-(5) are (111), (200), (220), (311), and (222) of fcc Cu-Ag solid solution, respectively; (b) $d = 1.5 - 3 \mu\text{m}$, diffraction patterns containing both fcc Cu-Ag solid solution ($1.5 - 2 \mu\text{m}$) and Cu-Ag two phase nanolayering region ($2 - 3 \mu\text{m}$); (c) $d = 3 - 4.5 \mu\text{m}$, diffraction rings (1)-(9) are Ag(111), Cu(111)/Ag(200), Cu(200), Ag (220), Cu(220), Ag(311), Ag(222), Cu(311) and Cu(222), respectively, same as the index in Fig. 5(b).

Fig. 8 ND-SD cross-sectional STEM-HAADF images of $\text{Cu}_{90}\text{Ag}_{10}$ pre-annealed at **1023 K** ($d_p = 262$ nm) and worn against a SS440C disk. The depth of nanocomposite layer, which appear dark owing to its low average atomic number, varies from $0.2\ \mu\text{m}$ (a) to $\sim 4\ \mu\text{m}$ (b); note that the mixing between the top nanocomposite layer and the Cu/Ag nanolayered structure led to the insertion of patches of Cu/Ag nanolayers in the top layer.

Fig. 9 Left vertical axis: Evolution of the steady-state wear rate of Cu-Ag pins worn against a Cu-Ni-Sn bronze (square symbols) or against a SS440C stainless steel (disc symbols) as a function of the initial Ag precipitate size, (here controlled by varying annealing temperature prior to wear tests). Right vertical axis: Evolution of the bulk hardness (lozenge symbols) of the Cu-Ag pins prior to wear testing, as a function of the Ag precipitate size. Lines connecting symbols are only guide for the eye (color online).